Journal of Science and Technology, Vol. 10 No. 4 (2018) p. 21-27

Development of Polyvinyl Alcohol/Chitosan Hydrogel Loaded with Fertilizer Compound: Preparation, Properties and Effect on Seed Germination

Nadirul Hasraf Mat Nayan[1,2*], Mohd Syahir Anwar Hamzah[2], Abdussalam Al-hakimi Mohd Tahir[2], Amirah Anis Afina Rajali[2], Eva Fariska Muslih[2], and Ruzaini Mazlan[2]

[1*]Microelectronics and Nanotechnology-Shamsuddin Research Centre (MiNT-SRC), Universiti Tun Hussein Onn Malaysia, 86400 Parit Raja, Johor, Malaysia.
[2]Faculty of Engineering, Universiti Tun Hussein Onn Malaysia, Higher Education Hub Pagoh, KM1 Jalan Panchor, 84600 Pagoh, Johor, Malaysia.

Received 15 September 2018; accepted 1 December 2018; available online 30 December 2018

DOI: https://10.30880/jst.2018.10.04.004

Abstract: This work reports the reinforcement of polyvinyl alcohol (PVA) hydrogel with chitosan as potential superabsorbent (SAP) fertilizer. The PVA/Chitosan hydrogel was prepared using superficial freeze thawing method. Mechanical properties and swelling ratio of the SAP hydrogels were optimum at 6 wt% of chitosan loading. Morphological analysis of the PVA/Chitosan hydrogel revealed excellent crystal like structure distribution and smooth of the surface due to good compatibility between the materials. The water retention of soil containing PVA/Chitosan hydrogel was also examined. It was found that the SAP hydrogel increased the water retention soil and sand at capacity 48.21 and 48.24 % respectively after 15 days. The influence of the SAP hydrogel on seed germination was observed using Okra seeds. The seeding has higher germination energy when the PVA/Chitosan hydrogel incorporated with the soil compared with soil without aid of SAP hydrogel. This is a good indication of the prepared SAP hydrogel for controlled release fertilizer.

Keyword: Hydrogel; superabsorbent polymer; fertilizer; plant growth; seed germination.

1. Introduction

The growing world population demands increasing food production. According to the projections of the United Nations Food and Agricultural Organization, the production of cereals will increase by 60% from 2000 to 2050. More crops means requirement of more plant nutrients. As a consequence also, fertilizer consumption will increase considerably. According to Food and Agriculture Organization (2006) fertilizers are applied to balance the gap between the permanent export of nutrients from the field with the harvested crops and the nutrients supplied by the soil. However, not all of the applied fertilizer ends up in the crop. Part of the fertilizer nutrients are lost to the wider environment and contribute to environmental problems such as loss of biodiversity or climate change.

One method of reducing fertilizer nutrient losses involves the use of slow or controlled release fertilizers [1]. Recently, the use of slow release fertilizers is a new trend to save fertilizer consumption and to minimize environmental pollution. There are three types of fertilizers which are slightly soluble materials (urea-formaldehyde), materials for deep placement (urea supergranules) and coated fertilizers [2-3]. Coated fertilizers are physically prepared by coating granules of conventional fertilizers with various materials that reduce their dissolution rate. The release and dissolution rates of water-soluble fertilizers depend on the coating materials [4].

Fertilizer and water are important factors that limit the production of agriculture, so it is extremely important to improve the utilization of water resources and fertilizer nutrients which are the highest variable costs items in crop production budget [5]. Fertilizer management for agriculture cultivation is very important because of the need to maintain fertility of the soil and to as well minimize soil erosion and nutrient loss [6]. The release of nitrogen fertilizers through the coated barrier could be enhanced by crosslinking hydrophilic network that are capable of holding large amount of water in the swollen state.

*Corresponding author: nadirul@uthm.edu.my

e-ISSN: 2600-7924/penerbit.uthm.edu.my/ojs/index.php/jst

Crosslinking is a common way to improve the controlled-release properties and mechanical strength by introducing a three-dimensional network structure [7-8].

Superabsorbent (SAP) manufacturers have focused their attention to develop biodegradable SAPs in order to fulfill the growing demand for biodegradable fertilizer products [8]. SAPs are a class of three-dimensional, hydrophilic, functional polymeric network systems with the ability to absorb large amounts of water, including those with good water retention capacity even under high pressure or temperature [9-10]. Polyvinyl alcohol (PVA) is a potential synthetic polymer that has good physical properties, high hydrophilicity, processability, and biodegradable that widely used in agriculture industry to deliver fertilizer, pesticides, herbicides and fungicides [11-12]. However, due to low mechanical properties it could lead to uncontrolled release of fertilizer in soil [13].

Chitosan is a highly deacetylated derivative of chitin, one of the most abundant natural and biodegradable polymers. It has been widely applied in the biomedical, pharmaceutical, and agricultural fields. The applications of chitosan are quite attractive due to its biodegradability, biocompatibility, nontoxic and widely used as reinforcement material [8,14-15]. Therefore it is suitable to be incorporated with PVA to improve mechanical properties and ideal to create slow release SAP hydrogel formulation.

In this study, the SAP fertilizer hydrogels were prepared from chitosan and polyvinyl alcohol using freeze thawing technique with glutaraldehyde as a crosslinker. The hydrogel will be characterized in terms of mechanical, swelling, morphological and water retention properties to select the optimum formulation. An experiment using the SAP for the germination of okra seeds and the growth of young plants showed satisfactory results.

2. Methodology

2.1 Preparation of PVA/Chitosan hydrogel loaded with fertilizer compound

The hydrogel was prepared using simple freeze thawing method. Polyvinyl alcohol, M_w 89,000-98,000 (Sigma Aldrich) was dissolved in 100 mL distilled water to produce 10% w/v polymer solution at 60^{o}C. Chitosan (Mercks) powders (2, 4, 6, 8, 10 wt% of PVA) were diluted in the acetic acid and charged into the PVA polymer solution. 6 mL of glutaraldehyde (Sigma Aldrich) and 10 mL of NPK fertilizer solution (Jabatan Pertanian Ayer Hitam, Malaysia) were mixed into the PVA-Chi solution until homogenous. The hydrogel solution will be poured into the mould and subjected to 3 cycles of freezing at -20^{o}C for 24 hours and thawing at room temperature for 24 hours.

2.2 Characterization

2.2.1 Mechanical testing

The compression test of the hydrogel was performed using dynamic mechanical analyser (TA instrument). The samples were tested at temperature 23°C and 50% relative humidity with compressive ramp up to 60% strain at a strain rate of 10% min-1.

2.2.2 Swelling ratio

The samples were immersed in phosphate buffered saline (PBS) solution for 24 hours, the swollen weight of the hydrogel sample (W_t) was recorded, and then the samples were removed from the swelling medium and dried in vacuum at 60°C for at least 48 hours to a constant mass (W_d). The swelling ratio was calculated on the basis of Eq. (1).

$$Swelling\ ratio\ (\%) = \frac{W_t}{W_d}\ x\ 100 \qquad (1)$$

Five samples were tested for each set of hydrogels (n= 5).

2.2.3 Scanning electron microscope

The surface morphologies of hydrogel was examined using a scanning electron microscope (Leo Supra 50VP Field Emission SEM, Carl Zeiss, Germany) with the magnification of 100 to 300 times of origin specimen at 5 kV of accelerating voltage

2.2.4 Water retention capacity

A 100 g of dry sand was mixed with 1 g hydrogel and placed in a cup (Sample A) and another cup without hydrogel as a control (Sample B). 300 mL of water was added into each cups and incubated at room temperature for 15 days. The initial mass of the mixture in the cups was measured (W_i), and then the weight of cups was measured daily (W_t) to calculate the water retention of hydrogel using Eq. (2).

$$Water\ retention\ (\%) = \frac{W_t}{W_i} \text{x } 100 \qquad (2)$$

Five samples were tested for each set of hydrogels (n= 5).

2.3 Germination and Growth Analysis

2.3.1 Seed germination test

The effects of fertilizer hydrogel on seed germination and early-stage seedling growth were investigated by growing okra. Moisture soil was placed into two identical rectangular trays at 6 cm depth. One tray was irrigated with water with fertilizer hydrogels and the other one without SAP fertilizer hydrogels. The same amount (100 pieces) of healthy okra seeds was placed in each tray. Germination energy (GE) was calculated using Eq. (3) to compare the effect of the soil on seed germination. Plant growth variables, such as plant height, root length, fresh weight, and dry weight were measured after 15 days of seedling growth.

$$Germination\ Energy\ (\%) = \frac{S_t}{\mathrm{S_i}} \times 100 \qquad (3)$$

Where S_t represent amount of germinated seeds in first 3 days and S_i represent initial total number of seed. Five samples were tested for each set of hydrogels (n= 5).

3. Result and Discussion

3.1 Mechanical properties

The mechanical properties of hydrogels are important criteria that will affect swelling behavior of the system. As can be seen in Table 1, addition of chitosan until improves mechanical behavior of the hydrogel. The crosslink between amine groups in chitosan with carbonyl group in cross linker might be increased by increasing the concentration. Hence, not only the mechanical properties of this hydrogels are better, but also the structure becomes stronger and denser.

Table 1 Compressive modulus and swelling ratio of PVA/Chitosan hydrogel.

Samples	Compressive modulus (kPa)	Swelling ratio (%)
PVA	13±0.3	37.9
PVA/2%Chitosan	17±0.2	44.4
PVA/4%Chitosan	28±0.4	47.8
PVA/6%Chitosan	37±0.1	58.3
PVA/8%Chitosan	39±0.3	51.2
PVA/10%Chitosan	42±0.2	45.7
Chitosan	15±0.3	33.2

3.2 Swelling ratio

The water absorbency of PVA/Chitosan hydrogels in form of swelling ratio is shown in Table 1. The data represented is the equilibrium swelling ratio after 24 hours. The water absorbency of PVA/Chitosan hydrogel increase until 6% chitosan content. However, the high amount of chitosan (8 and 10 %) reduces the absorbency behavior due to mechanical structure that is more rigid and denser result from crosslinking reaction. The addition of hydrophilic group from Chitosan is responsible for swelling properties of the hydrogel. Based on the mechanical and swelling behaviour, PVA/6%Chitosan hydrogel (also referred as SAP hydrogel) was selected for further characterization to determine its effect towards plant seed germination.

3.3 Morphological properties

Fig. 1 depicts the SEM morphology of the PVA, PVA/6%Chitosan and Chitosan hydrogel. Surface of the PVA/6%Chitosan (Fig. 1b) revealed even distribution of the crystal like surface compred to smooth surface of the PVA (Fig. 1a) and chitosan (Fig. 1c). The rough outer layer of PVA/6%Chitosan gives extra surface area that able to absorb large amount of water. The addition of chitosan would reduce water diffusion into inner core of hydrogel and NPK diffusion outside, which provided good control release behaviour.

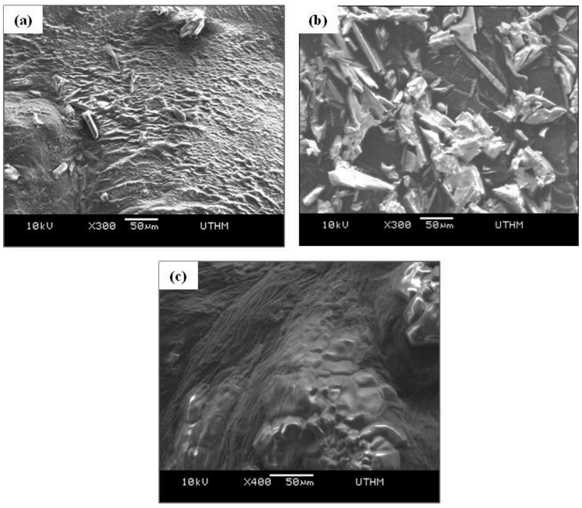

Fig. 1 SEM image of (a) PVA hydrogel, (b) PVA/6%Chitosan hydrogel and (c) chitosan hydrogel.

3.4 Water retention capacity

The most important application of SAP is for agriculture and horticulture, especially for saving water in dry and desert regions and for accelerating plant growth. So, it is necessary to investigate the water-retention ability of SAP fertilizer hydrogel in sand and soil. Fig. 2 shows the water retention of sand with and without PVA/6%Chitosan SAP hydrogel. The masses of sand with and without SAP were compared within 15 days. From Fig. 2, the addition of SAP fertilizer hydrogel to sand could obviously increase the water-retention. The mass of sand decreased with an increased incubation time at room temperature. The decreasing trend of sand without SAP is higher than that in sand with SAP. After 15 days, the mass of sand without SAPs was nearly 41%, but that of the sand with SAP was 48%.

Fig. 3 shows the water retention of soil mixed with SAP and soil without the SAP. The rate of water loss increased with increased incubation time. It is clear that soil mixed with SAP can hold more water than soil without SAP. The water holding capacity of the soil increased with an increased amount of SAP in the soil. After 18 days, the mass of soil without SAP was ~40%, 45% for soil with SAP sample B and 48% with SAP sample A.

From this study, it could be inferred that SAP fertilizer hydrogel had good water-retention capacity in soil, and that with SAP fertilizer hydrogel use water can be saved and managed so that they can be effectively used for the growth of plant. These were the significant advantages over the normal slow release fertilizers, which always only had a controlled-release property. The reason was that the SAP fertilizer hydrogel could absorb and store a large quantity of the water in soil, and allow the water absorbed in it to be slowly released with the decrease of the soil moisture.

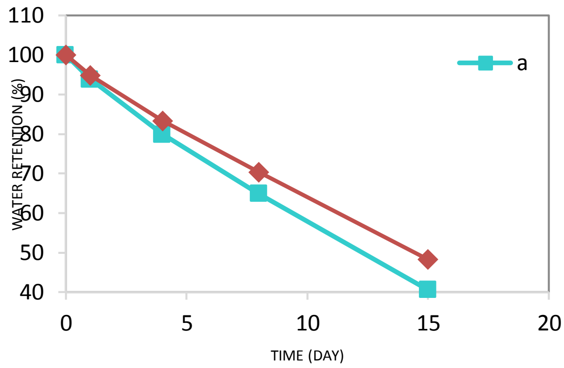

Fig. 1 Effect of standing time of SAP in sand on water retention, (a) water + dry sand without SAP; (b) water + dry sand + SAP fertilizer hydrogel.

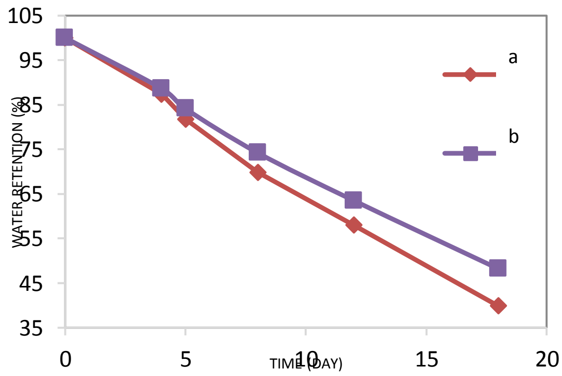

Fig. 2 Water retention of soil with SAP fertilizer hydrogel. (a) water + dry soil without SAP; (b) water + dry soil + SAP sample A.

Simultaneously, nutrition could also be released slowly with the water. Therefore, the swollen SAP fertilizer hydrogel was just like an additional nutrient reservoir for the plant–soil system and thus could increase the utilization efficiency of water and fertilizer at the same time. Furthermore, as we known, the chitosan material was a biodegradable material so the hydrogel was not harmful to the soil [16]. Thus there would be a good use potentiality in dry-prone regions.

3.5 Effect of PVA/Chitosan hydrogel on seed germination

The application of the SAPs in agriculture was studied for the purpose to promote plant growth [17-18]. In this study, the synthesized SAPs were used agriculturally to determine the effect on the germination of okra seeds and on the growth of young plants. Based on Fig. 4, all seeds used in the experiment were healthy and planted at random, and were found that the germination energy of the seeds in soil with SAP fertilizer hydrogel was obviously higher than that of the seeds in soil without SAPs. This is likely because the SAPs not only can absorb large amounts of water but also have good water retention capability, which supplies plentiful water to promote plant growth. After a few days, soil with SAP fertilizer hydrogel showed a positive effect on the length and weights of the okra plants as shown in Table 2 and Table 3.

Table 2 Effect of the SAP fertilizer hydrogel on germination of the okra seeds (after 3 days)

Samples	Germination energy (%)
Control	13±0.3
PVA/6%Chitosan (SAP hydrogel)	17±0.2

Table 3 Effect of SAP fertilizer hydrogel on growth of the okra plants (after 15 days).

Samples	Control	PVA/6%Chitosan
Height of the plant (cm)	8.5±0.1	10.5±0.1
Length of the root (cm)	4.5±0.1	10±0.1
Weight of fresh plant (g)	0.394±0.001	0.548±0.001
Dry weight of plant (g)	0.030±0.001	0.048±0.001

In previous studies, carboxy-methylcellulose (CMC)/Acrylic acid (AAc) blended SAP showed a considerable effect on the germination of wheat seeds and young plant growth [19]. Superwater absorbent obtained from cassava starch/acrylic acid blend showed a good effect on the growth of Chinese cabbage [20]. Based on finding, it can be concluded that the SAPs have a potential application in agriculture, especially in arid and desert regions.

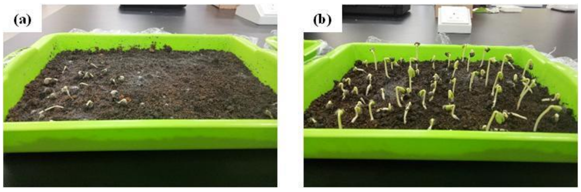

Fig. 4 The seed germination of okra plants after five days (a) control and (b) PVA/6%Chitosan (SAP hydrogel).

4. Conclusion

Incorporation of chitosan has successfully improved the mechanical properties of the PVA hydrogel. Swelling ratio of PVA/Chitosan hydrogel showed highest equilibrium water absorbency (58.3%) at 6 wt% chitosan. In agriculture, these properties are important during irrigating or raining for water absorption and physical endurance. Morphological examined revealed high surface area for water absorption and smooth layer for control release action of NPK fertilizer. After 15 days, the water retention of sand and soil containing PVA/Chitosan were higher compared to non-containing SAP hydrogel. The seed germination analysis on Okra seed showed better germination energy and well growth of young plant by utilize SAP hydrogel in the soil. Though works have been done, further investigation is needed to study the effect of the SAP on plant growth and the kinetic release model of the fertilizer to the soil.

Acknowledgements

The authors would like to express the deepest appreciation to the Universiti Tun Hussein Onn Malaysia (UTHM), for funding this project through (Geran Penyelidikan Pascasiswazah-Vote number U993).

REFERENCES

[1] Akelah, A. (1996). Novel utilizations of conventional agrochemicals by controlled release formulations, *Materials Science and Engineering: C*, Vol. 4. No. 2 pp. 83-98.

[2] Roy, A., Bajpai, J., & Bajpai, A. K. (2009). Dynamics of controlled release of chlorpyrifos from swelling and eroding biopolymeric microspheres of calcium alginate and starch, *Carbohydrate Polymers*, Vol. 76. No. 2 pp. 222-231.

[3] Azwa, Z. N., Yousif, B. F., Manalo, A. C., & Karunasena, W. (2013). A review on the degradability of polymeric composites based on natural fibres, *Materials & Design*, Vol. 47 pp. 424-442.

[4] Jin, S., Yue, G., Feng, L., Han, Y., Yu, X., & Zhang, Z. (2010). Preparation and properties of a coated slow-release and water-retention biuret phosphoramide fertilizer with superabsorbent, *Journal of Agricultural and Food Chemistry*, Vol. 59. No. 1 pp. 322-327.

[5] Campos, E. V. R., de Oliveira, J. L., & Fraceto, L. F. (2014). Applications of controlled release systems for fungicides, herbicides, acaricides, nutrients, and plant growth hormones: A review, *Advanced Science, Engineering and Medicine*, Vol. 6. No. 4 pp. 373-387.

[6] Bah, A., Husni, M. H. A., Teh, C. B. S., Rafii, M. Y., Syed Omar, S. R., & Ahmed, O. H. (2014). Reducing runoff loss of applied nutrients in oil palm cultivation using controlled-release fertilizers, *Advances in Agriculture*, 2014.

[7] Chen, C., Gao, Z., Qiu, X., & Hu, S. (2013). Enhancement of the controlled-release properties of chitosan membranes by crosslinking with suberoyl chloride, *Molecules*, Vol. 18. No.6, pp. 7239-7252.

[8] Wu, L., Liu, M., & Liang, R. (2008). Preparation and properties of a double-coated slow-release NPK compound fertilizer with superabsorbent and water-retention, *Bioresource Technology*, Vol. 99. No. 3 pp. 547-554.

[9] Rosa, F., Bordado, J. M., & Casquilho, M. (1992). Polímeros superabsorventes potencialidades e aplicações, Química Nova.

[10] Morgan, K. T., Cushman, K. E., & Sato, S. (2009). Release mechanisms for slow- and controlled-release fertilizers and strategies for their use in vegetable production, *Hort Technology*, Vol. 19. No. 1 pp. 10-12.

[11] Doria-Serrano, M. C., Ruiz-Trevino, F. A., Rios-Arciga, C., Hernandez-Esparza, M., & Santiago, P. (2001). Physical characteristics of poly (vinyl alcohol) and calcium alginate hydrogels for the immobilization of activated sludge, *Biomacromolecules*, Vol. 2. No. 2 pp. 568-574.

[12] Gaaz, T. S., Sulong, A. B., Akhtar, M. N., Kadhum, A. A. H., Mohamad, A. B., & Al-Amiery, A. A. (2015). Properties and applications of polyvinyl alcohol, halloysite nanotubes and their nanocomposites, *Molecules*, Vol. 20. No. 12 pp. 22833-22847.

[13] Pająk, J., Ziemski, M., & Nowak, B. (2010). Poly (vinyl alcohol)–biodegradable vinyl material, *Chemik*, Vol. 64. pp. 523-530

[14] Dutta, P. K., Dutta, J., & Tripathi, V. S. (2004). Chitin and chitosan: Chemistry, properties and applications.

[15] Badawy, M. E., & Rabea, E. I. (2011). A biopolymer chitosan and its derivatives as promising antimicrobial agents against plant pathogens and their applications in crop protection, *International Journal of Carbohydrate Chemistry*, 2011.

[16] Borzacchiello, A., Ambrosio, L., Netti, P. A., Nicolais, L., Peniche, C., Gallardo, A., & San Roman, J. (2001). Chitosan-based hydrogels: synthesis and characterization, *Journal of Materials Science: Materials in Medicine*, Vol. 12. No. 10-12 pp. 861-864.

[17] Raju, K. M., Raju, M. P., & Mohan, Y. M. (2003). Synthesis of superabsorbent copolymers as water manageable materials, *Polymer International*, Vol. 52. No. 5 pp. 768-772.

[18] Nnadi, F., & Brave, C. (2011). Environmentally friendly superabsorbent polymers for water conservation in agricultural lands, *Journal of Soil*

Science and Environmental Management, Vol. 2. No. 7 pp. 206-211.

[19] Sutradhar, S. C., Khan, M. M. R., Rahman, M. M., & Dafadar, N. C. (2015). The synthesis of superabsorbent polymers from a carboxymethylcellulose/acrylic acid blend using gamma radiation and its application in agriculture, *Journal of Physical Science*, Vol. 26. No. 2 pp. 23.

[20] Dafader, N. C., Duoc, N. T., Hong, P. T. T., & Binh, D. (2013). Synthesis and Characterization of Superwater Absorbent Hydrogel from Cassava Starch and Acrylic Acid Blends by the Application of γ-Radiation, *Caspian Journal of Applied Sciences Research*, Vol. 2. No. 1.